

The model of the ideal crystal as a criterion for evaluating of the approximate equations of the liquids.

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Abstract

It is necessary for the statistical description of collective effects in liquids to set that or other approximation between direct and pair correlation functions which describe a neighboring order. The analytical solution of the generalized Ornstein-Zernike (OZ) equation was obtained for a system of particles at $T = 0$. It is shown that in this limit case the neighboring order disappears and the direct correlation function describes a distant order which is typical for the ideal crystal. The approximation correctly describing the limit transition liquid-solid at $T = 0$ will have a physical meaning.

Introduction

The structure and thermodynamics of both dense gases and liquids is described by a pair correlation function h_{12} considering the collective effects in dense mediums. Nowadays about 20 approximate integral equations of the Ornstein-Zernike (OZ) type connecting the direct C_{12} and pair h_{12} correlation functions are proposed for describing of the above-mentioned one [1, 2]. The degree of exactness of every such approximation is impossible to be evaluated. The physical meaning of

their basic approximations has not been cleared up to the end yet. Thus such a situation suggests a choice of maximum exact approximations in a comparison with the result achieved at the numerical experiment. Nevertheless such a comparison doesn't reveal the physical meaning of approximations.

The OZ equation is to be used for the spatial homogenous and isotropic mediums as in such a case a two-particle distribution function (as well as a pair correlation function) depends only on a mutual distance between the particle centers r_{12} , that makes all the calculations much more simplified.

But there exists a more generalized form of the OZ equation for the spatial inhomogenous anisotropic mediums [3, 4, 5]. It has not been used widely yet for the solution of more exact problems. One can mention its use only for the description of the liquid-solid phase transition [5, 6]. This work describes the use of the Martynov-Sarkisov approximation, which gives the best agreement with the data of the numerical experiment for the hard spheres system [5].

In this work we suggest using the generalized OZ equation for the description of the ideal crystal at $T = 0$. The pair correlation function h_{12} in this limit case takes the meaning of the Dirak δ function. As a result, a linear integral equation for the direct correlation function is achieved, which has a simple analytical solution. It should fit The results known from crystallophysics for the ideal crystal. So the limit transition to the model of the ideal crystal may be considered as a physical criterion for the evaluation of the exactness for the approximations used in physics of liquids.

1 Initial equations

In works [3, 5, 7] it was shown that a hierarchy of Bogolubov- Born-Green-Kirkwood-Yvon (BBGKY) equations may be modified into a two equations system

$$\omega_1 = n \int G_2 S_{12} d(2) + \ln a \quad (1)$$

$$h_{12} = C_{12} + n \int G_3 C_{13} h_{23} d(3) \quad (2)$$

for two unknown functions: a one-particle distribution function $G_1(\vec{r}_1) = \exp(\omega_1(\vec{r}_1))$ and a two-particle distribution function

$$G_{ij}(\vec{r}_i, \vec{r}_j) = G_i G_j (1 + h_{ij}), \quad (3)$$

$$h_{ij} = -1 + \exp\left(\frac{-\Phi_{ij}}{\Theta} + \Omega_{ij}(\vec{r}_i, \vec{r}_j)\right), \quad (4)$$

where $n = N/V$ is density, Φ_{ij} -molecular interaction potential, $\Theta = kT$ -temperature, $d(i) = d\vec{r}_i$ - a volume integral element of the i particle.

All previous distribution functions are expressed through G_1 and G_{12} . The direct correlation functions S_{ij} , C_{ij} in equations (1) and (2) are evidently expressed through infinite integral sets distinguished from the products of the pair correlation functions h_{ij}

$$S_{ij} = h_{ij} - \Omega_{ij} - \frac{1}{2}h_{ij}(\Omega_{ij} + \frac{1}{6}M_{ij}^{(1)}), \quad (5)$$

$$C_{ij} = h_{ij} - \Omega_{ij} + \frac{1}{2}M_{ij}^{(2)}, \quad (6)$$

in which

$$M_{ij}^{(k)} = n^2 \int \int G_3 G_4 h_{i3} h_{i4} h_{34} h_{3j} h_{4j} d(3) d(4) + \dots, k = 1, 2 \quad (7)$$

the so-called bridge-functionals represent infinite sums of non-reduced diagrams.

For spatial homogeneous and isotropic systems (dense gases and liquids) at $\omega_1 = 0$, $G_1 = 1$, $G_{12} = G_{12}(\vec{r}_{12})$, equation (1) is a definition of the activity factor logarithm $\ln a$. Equation (2) describing the neighboring order in liquids tends to come to a well-known OZ ratio

$$h_{12} = C_{12} + n \int C_{13} h_{13} d(3), \quad (8)$$

being the basis of the modern theory of liquids and molds [1, 2]. For making ratio (8) closed it is necessary to set an approximation connecting the direct correlation function $C_{12}(\vec{r}_{12})$ with the pair correlation function $h_{12}(\vec{r}_{12})$.

2 The ideal crystal

One particle distribution function has the meaning of local density in laboratory coordinate system. For spatially homogeneous isotropic mediums one particle distribution function equals one because the external field does not exist. For the crystal condition one particle distribution function does not equal one, even if the external field does not exist. To describe such a system it is necessary to introduce the external field according to Bogolubov which fixes the crystal place in the space and then to make it tend to zero. Then one particle distribution function describes the local density distribution in the regard to the fixed coordinate system giving the crystal place as a whole. As an origin of such a coordinate system it is convenient to choose one of lattice particles giving it number zero conditionally. Therefore one particle distribution function $G_1 = \exp(\omega_1)$ for the crystal can be represented in the form of the periodic function

$$G_1(\vec{r}_1) = \sum_{\vec{k}} G_{\vec{k}} \exp(i\vec{k}\vec{r}_1), \quad (9)$$

For the ideal crystal at $T = 0$ every Fourier's component $G_{\vec{k}}$ is similar and G_1 is a superposition of three-dimension Dirak δ functions

$$G_1(\vec{r}_1) = \sum_{\vec{r}_n} \delta(\vec{r}_1 - \vec{r}_n) \quad (10)$$

where the summation is done by crystal lattice nodes \vec{r}_n . whose coordinates, in their turn, must be defined.

The mutual arrangement of lattice nodes (that is the lattice period and the type of the crystal system) is defined by the potential of molecular interaction. On the other hand, the potential Φ_{12} enters the pair correlation function in the form of the combination $-\frac{\Phi_{12}}{\Theta}$. Let us consider the kind of the function h_{12} at $T = 0$. Let the molecular interaction be described by Lenard-Jones potential

$$\Phi_{12} = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6], \quad (11)$$

where σ is a characteristic size of a molecule. The potential Φ_{12} has a minimum at the point $r_0 = \sigma\sqrt[6]{2}$. Therefor the function $-\frac{\Phi_{12}}{\Theta}$ at $T \rightarrow 0$

has δ -shaped maximum at this point. That is why one can neglect the thermal potential ω_{12} describing the neighbouring order. As a result h_{12} is approximated one-dimension Dirak function $\delta(r_{12} - r_0)$.

As a result at $T = 0$ we get the following equation for the straight correlation line with regard to (10)

$$C_{12}^{(2)} + n \sum_{\vec{r}_n} C_{12}^{(2)}(\vec{r}_1, \vec{r}_n) \delta(r_{2n} - r_0) = \delta(r_{12} - r_0). \quad (12)$$

We notice that (12) is the linear equation whose solution is sought in the form

$$C_{12} = \alpha \delta(r_{12} - r_0), \quad (13)$$

where α is a coefficient to be defined. Substitution C_{12} in (12) results in the following expression

$$\delta(r_{12} - r_0) = \alpha \delta(r_{12} - r_0) + n \alpha \sum_{\vec{r}_n} \delta(|\vec{r}_1 - \vec{r}_n| - r_0) \delta(|\vec{r}_2 - \vec{r}_n| - r_0). \quad (14)$$

Particles 1 and 2 are the neighbouring ones. The summation is done by those nodes which are the nearest both for the first particle and for the second one. Let such particles have N_0 numbers. Using (14) we get

$$\alpha = \frac{1}{1 + nN_0}, r_{12} = r_0, r_{13} = r_0, r_{23} = r_0 \quad (15)$$

The correlation (15) defines the crystal structure (the lattice period and the type of the crystal system). For determining the crystal system we should calculate the number N_0 .

At $T = 0$ the system is densely packed. There are two types of lattices with the dense packing - face centered cubic and hexagonal lattices [8]. Their structure is formed by successive layers of densely packed planes. Every particle has twelve neighbouring particles. This structure type is connected with the distant order in the crystal. But in any substance (including the crystal) there is the neighbouring order which is described by the second addend in the right-hand side (14) in this case.

Let us take arbitrarily a couple of the neighbouring particles arranged in the plane (111). It has four particles juxtaposed with it for

both types of the lattice: two particles in the plane (111) and one particle in every adjoined plane. If particles 1 and 2 lie in two neighbouring planes the situation is different. For the face centered cubic lattice N_0 is 4 as before but for the hexagonal lattice N_0 is 3. So $N_0 = \text{const}$ for the face centered cubic lattice. As the pair of the neighbouring particles is chosen arbitrarily this indicates that the face centered cubic lattice is realized. It corresponds to the experimental data for crystals of inert gases. However for Lenard-Jones potential the hexagonal structure has much lower energy than the face centered cubic lattice therefor it is this lattice that must be realized. The problem of the crystal system is not solved in this paper yet.

Now we show that solutions (10) and (13) satisfy the equation (1). The direct correlation function $C_{12}^{(1)}$ neglecting two particle correlations ω_{12} equals

$$C_{12}^{(1)} = C_{12}^{(2)} = \alpha \delta(r_{12} - r_0). \quad (16)$$

Substitution this expression in (1) we shall get

$$\omega_1 = n\alpha \sum_{\vec{r}_n} \delta(|\vec{r}_1 - \vec{r}_n| - r_0) + \ln a. \quad (17)$$

Let $a = 1$ and doing summation by \vec{r}_{12} as it is done in (14)

$$\omega_1 = n\alpha N_0 \delta(|\vec{r}_1 - \vec{R}_0| - r_0) + \ln a. \quad (18)$$

where \vec{R}_0 is a radius of the vector-particle placed in the coordinate system origin. Since coordinates of all the nodes are known now, ω_1 is a given function G_1 can be given in the form (10).

The complicity of problems being solved by the physics of condensed matter makes one use different physically based approximations. In particular, in the physics of plasma and solids an approximation of the self-coordinated field is widely used.

In the physics of liquids a superpositional approximation is well-known, which is used to express a triple function of the distribution through two-particle ones. It is to the superpositional approximation, that fits to the hypernetted chain equation, which results from (2) by the neglect of all the irreducible diagrams. Summing up of such diagrams is practically unrealizable. Physically it is connected with the

fact that at the limit temperatures it is necessary to take into account the collective effects, stimulated by a molecular motion. That is why it is necessary to offer a physical value criterion of the irreducible diagrams.

A limit transition to the ideal crystal at $T = 0$ represent such a criterion. In this case it is possible to neglect the collective effects connected with the molecular motion. As a result a limit ratio for the direct correlation function C_{12} , that effectively includes a contribution of the irreducible diagrams, is possible to be obtained.

From a great number approximations between C_{12} and h_{12} the most physically valid is that one which fits to the given limit ratio.

Conclusion

The solution of Ornstein-Zernike generalized equation is obtained for the ideal crystal at $T = 0$. In this case the pair correlation function h_{12} Degenerates to Dirak δ function and for the direct correlation function C_{12} the linear integral equation is found which has the analytical solution. By using it the main problem of physics of liquids is solved - establishment of closure between the direct and pair correlation functions.

At the same time there is still a problem for the aggregate condition, the method developed by us can be used as a criterion for evaluating the closures: those resulting in the solution for the ideal crystal at $T = 0$ will have the physical meaning.

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